Nitric Acid Uptake and Decomposition on Black Carbon (Soot) Surfaces: Its Implications for the Upper Troposphere and Lower Stratosphere

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Abstract The uptake and decomposition of HNO_3 on black carbon (soot) surfaces were investigated in order to evaluate the proposal that HNO_3 decomposition on aircraft-generated soot aerosols may alter the NO_x/NO_y partitioning in the upper troposphere and lower stratosphere. The experimental measurements were performed by using a fast flow-tube reactor coupled to a quadrupole mass spectrometer. Black carbon samples used as surrogate material for aircraft soot in this study included Degussa FW2, graphite, hexane soot, and kerosene soot. The measurements of uptake were performed by varying $P(HNO_3)$ in the range of $5 \times 10^{-7} \sim 5 \times 10^{-4}$ Torr at 220 K and 295 K. The results are summarized as follows. (1) Significant HNO_3 decomposition was observed on FW2 at 295 K with $P(HNO_3) \geq 1 \times 10^{-4}$ Torr while it did not occur at 220 K. Similar HNO_3 decomposition behavior on graphite was also observed under the condition of $P(HNO_3) \geq 10^{-4}$ Torr and T = 295 K although the extent of the decomposition was much smaller than on FW2. The decomposition of HNO_3 on soot produced NO, NO_2, H_2O,

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oxidized soot surface, and some unidentified volatile products. A bimolecular HNO_3 decomposition mechanism on soot surface was proposed in order to explain the observed decomposition behavior at higher partial pressures of HNO_3. On the other hand, HNO_3 immediately decomposed on FW2 surface at 503 K even at lower partial pressure (~10^{-6} Torr). (2) On flame-deposited hexane and kerosene soot film, no HNO_3 decomposition was observed up to $P(HNO_3) = 5 \times 10^{-4}$ Torr. The uptake and desorption of HNO_3 were reversible at 295 K and irreversible at 220 K. Adsorbed HNO_3 molecules on hexane soot film were saturated to a monolayer coverage at $P(HNO_3) \sim 2 \times 10^{-4}$ Torr according to Langmuir adsorption isotherm; further increase in $P(HNO_3)$ resulted in multilayer adsorption. (3) Under the experimental conditions ($P(HNO_3) = 5 \times 10^{-7}$ Torr and T = 220 K) mimicking the upper tropospheric environments, the uptake of HNO_3 was found to be purely physical adsorption without showing any sign of irreversible decomposition over all black carbon samples tested in this study. Subsequent heating of the sample following the uptake at 220 K desorbed most of the adsorbed HNO_3 molecules. However, heating well above room temperature decomposed adsorbed HNO_3 to give NO_x and some volatile products. (4) The uptake coefficients (γ_g) of HNO_3 on FW2 and kerosene soot were measured to be 0.067 and 0.060 at 295 K; 0.13 and 0.093 at 220 K, respectively, on the basis of the geometric area of the reactor coated with soot. Moreover, the measured uptake coefficients at 295 K were strongly dependent on the exposure time while those at 220 K were not. Finally, the present results suggest that the HNO_3 decomposition on soot aerosols through a direct gas-solid interaction, which was proposed as a possible NO_y-reactivation mechanism in the atmospheric modeling, should be dismissed. Alternative

mechanism for HNO_3 decomposition on liquid/soot interface is proposed for further laboratory study.

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